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LABORATORY OZONATION OF MUNICIPAL WASTEWATERS

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Variable amounts of organic nitrogen and ammonia were oxidized at pH 7.0 by ozone to nitrate. Organic nitrogen and ammonia oxidation to nitrate increased with increased pretreatment (lower initial COD in the wastewater) and increased pH. Nitrate residuals formed by the oxidation of ammonia and or organic nitrogen at the 70% COD removal level were less than 3 mg/l. The ozone distribution ratio between oxidation of the NOD and COD, and the COD removals as a function of ozone dose suggested that the relative order of oxidation was; easily oxidizable organic material, NH_3, TKN, and slowly oxidizable (nearly refractory) organic material. (EPA)

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ABSTRACT

Raw wastewater, secondary effluent, lime clarified and filtered raw and secondary wastewaters, carbon treated wastewaters, and breakpoint chlorinated plus carbon treated wastewaters were ozonated at pH 7.0 over a range of 5-90 minutes contact time. Ozonation of the raw wastewater, with high solids and COD content required impractical ozone dosages for appreciable COD removal. In all effluents, except raw wastewater, 100 mg/l of ozone produced at least a 70% COD removal. Organic oxidation efficiencies in the raw and secondary wastewaters, based upon one atom of available oxygen per molecule of ozone, exceeded 100% indicating that one or more atoms of the ozone molecule or molecular oxygen participated in the organic oxidation mechanism.

Variable amounts of organic nitrogen and ammonia were oxidized at pH 7.0 by ozone to nitrate. Organic nitrogen and ammonia oxidation to nitrate increased with increased pretreatment (lower initial COD in the wastewater) and increased pH. Nitrate residuals formed by the oxidation of ammonia and or organic nitrogen at the 70% COD removal level were less than 3 mg/l. The ozone distribution ratio between oxidation of the NOD and COD, and the COD removals as a function of ozone dose suggested that the relative order of oxidation was; easily oxidizable organic material, NH_3, TKN, and slowly oxidizable (nearly refractory) organic material.

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SECTION I

CONCLUSIONS

Ozonation at pH 7.0 of raw wastewater with high solids and high COD content required impractical ozone dosages (300 mg/l) for COD removals.

Ozonation at pH 7.0 of wastewater effluents from the EPA-DC Pilot Plant (secondary, lime clarified and filtered secondary, lime clarified and filtered raw wastewater, and carbon column effluent from the physical-chemical treatment system) reveal that reacting 100 mg/l or less of ozone with waters of low initial COD (50 mg/l) produced at least 70% COD removal in all effluents.

The addition of ozone beyond the 70% COD removal level produced only a very gradual COD decrease. In all tests, the COD never decreased to zero even at high ozone doses (200-300 mg/l O_3) and indicated the presence of ozone-oxidation resistant organic materials. It is not known if these oxidation resistant organic materials remaining in the wastewater were originally present or if they were a byproduct of ozonation.

Typical residual COD's at 70% removal for secondary, lime clarified and filtered secondary, lime clarified and filtered raw wastewater, and carbon column effluents from physical-chemical treatment of raw wastewater were 10.5 mg/l, 13.5 mg/l, 14.2 mg/l and 3.6 mg/l, respectively.

In ozonation of raw wastewater and secondary effluent the organic oxidation efficiency, based upon one atom of oxygen available per molecule of ozone, and for COD reduction of 70%, exceeded 100% of the available "active" oxygen in the ozone. The organic oxidation efficiencies in chemically clarified effluents avereaged 100% for the COD reduction of 70%. In the carbon column effluent with a low initial COD of 13 mg/l, the organic oxidation efficiency at the 70% COD reduction was 55%.

The observed organic oxidation efficiencies above 100% indicated that either molecular oxygen or the oxygen in the entire ozone molecule contributed to the oxidation mechanism.

Portions of the total organic carbon (TOC), were oxidized to carbon dioxide. Typically, the TOC removal was about one half of the COD removal.

Organic nitrogen and ammonia were also oxidized at pH 7.0 by ozone to nitrate. For any given ozone dosage the ozone consumed by the nitrogen oxygen demand (NOD) increased with increasing wastewater pretreatment. The total organic carbon and nitrogen oxidation efficiencies in all effluents except raw wastewater exceeded 100% at the 70% COD removal level. This confirmed that either molecular oxygen or the entire ozone molecule participated in the oxidation mechanism. The total oxidation efficiencies and ratios of ozone used for nitrogen oxidation to organic carbon oxidation indicated that the oxidation sequence, in the order of reactivity, was easily oxidized organic material, ammonia nitrogen, organic nitrogen and slowly oxidizable (nearly refractory) organic material.

Ozonation of carbon column effluents of low initial COD, containing ammonia and organic nitrogen, required greater amounts of ozone for the removal of COD and TOC than were required for the same carbon column effluent without ammonia. For example, in the non-chlorinated carbon column effluent (with ammonia) a COD removal of 40% was achieved with a residual COD of 6.7 mg/l at an applied ozone dose of 50 mg/l. In the breakpoint chlorinated carbon column effluent (without ammonia) a 55% COD removal was attained with a residual COD of 5.0 mg/l at the same applied dosage. The TOC removals similarly required less ozone in the absence of ammonia. In all cases, however, the removal of ammonia before ozonation did not permit complete oxidation of the COD.

Increasing the pH from pH 5 to 11 increased the transfer of ozone to the effluent. Above pH 9, COD removal was similar to that at lower pH's and additional ozone was used in ammonia and organic nitrogen oxidation.

SECTION II

RECOMMENDATIONS

Pilot studies of ozone transfer are needed to determine realistic transfer efficiencies and process costs.

Laboratory studies are needed to determine the types of residual organics remaining after ozonation.

Disinfection studies are needed to evaluate the removal of bacteria and virus.

SECTION III

INTRODUCTION

Ozone has been used for nearly a century in wastewater treatment primarily as a disinfectant (1, 2, 3, 4, 5,6).Ozone inactivates E. Coli, Poli virus, cysts of histolytica, spores, algae, and protozoa more rapidly than chlorine (7). Ozone exhibits an "all or nothing" action on bacteria in contrast to the linear relationship between chlorine and bacteria kill (2).

More recently, ozone has been used to control odor, taste and color in wastewater (2, 5, 6, 7, 8, 9, 10, 11, 12).

Ozone has also been successfully used to treat waters polluted by phenols and cyanides from industrial wastes (7, 13, 14, 15).

Although ozone reacts with dissolved organics in wastewaters to yield high quality water, it has not been used extensively in municipal wastewater treatment because of the relatively high cost of ozone, the lack of residual ozone in the wastewater (2), and a lack of knowledge of the effectiveness of ozone treatment. A recent study (16) of ozone treatment of clarified secondary wastewater revealed an average COD removal of 57% and an ozone oxidation efficiency, based on one atom of available oxygen per molecule of ozone, of 80%. For a 10 mgd plant, the treatment cost was estimated at 7.7 cents per 1,000 gallons.

The study described herein was undertaken to determine the dissolved organic removals and ozone oxidation efficiencies for ozonation of various municipal wastewaters and to evaluate the effect of ozone on the nitorgen content of these wastewaters.

The municipal wastewaters treated with ozone were raw wastewater, secondary effluent, lime clarified and filtered raw wastewater, lime clarified and filtered secondary effluent, carbon column effluents, and breakpoint chlorinated and carbon treated effluents. These effluents were obtained from the EPA-DC Pilot Plant in Washington, D.C.

SECTION IV

EXPERIMENTAL

The effluents were collected in eight liter batches. The wastewater pH was adjusted with H_2SO_4 or NaOH to 7.0 before ozonation at various contact times. Secondary effluents were also ozonated at pH's of 5, 9, and 11.

Ozone was generated by passing pure dry oxygen at a flow rate of 1.2 l/min through a silent discharge ozonator. Line voltage to the ozonator was kept constant to minimize variations in ozone production. A portion of the ozone-oxygen from the ozonator was continuously fed through two KI traps and a wet test meter to determine inlet ozone concentrations. The flow rate through the reactor averaged 0.65 liters per minute at 8 psi and 25°C. The ozone concentration in the gas fed into the system averaged 21.5 mg/l.

The oxygen-ozone mixture was introduced to the sample in a baffled reactor beneath turbine blades mixing at 500 rpm, to ensure complete dispersion of the gas throughout the sample. One liter aliquots of the eight liter grab samples were ozonated in the reactor for 5, 15, 30, 45, 60 and 90 minutes, respectively. Thus ozone transferred to the sample was a function of both the wastewater content, and the ozone contact time. Unreacted ozone and oxygen carrier gas passed from the reactor through two KI traps and a wet test meter. After ozonation, the system was flushed with helium for ten minutes to remove ozone and oxygen from the lines and sample. Samples of the ozonated wastewater in the reactor were then titrated for residual ozone to confirm complete ozone removal.

Variables used to evaluate ozone treatment of the wastewaters were COD, TOC, BOD_5, NH_3, TKN, $(NO_3 + NO_2)$, and ozone reacted. Organic oxidation efficiencies were calculated from the ratio of the change in COD in mg/l

to the amount of ozone reacted. The organic oxidation efficiencies (OOE) were calculated assuming that in each of the reacting ozone molecules, only one oxygen atom was available for the oxidation.

$$O.O.E. = \frac{COD\ mg/l\ \ (100)}{O_3\ reacted\ (1/3)\ mg/l} \qquad (1)$$

$$TOE = \frac{COD\ mg/l + NOD\ mg/l\ \ (100)}{O_3\ reacted\ (1/3)\ mg/l} \qquad (2)$$

As organic nitrogen may also be oxidized in the COD analysis, total oxidation efficiencies were only approximate.

The experimental system consisted of a Welsbach Laboratory Ozonator Model T-408, a Sola constant voltage transformer, a two-liter glass reaction kettle with a one inch double grid baffle attached to the side. The kettle top was welded to the kettle to prevent gas leakage. Mixing was achieved by an inverted turbine inserted in the bottom of the kettle, propelled by a heavy duty Waring commercial blender (Model CB-5) with a rheostat to control blender speed. Two wet test meters and four 500 ml gas washing tubes were used in the ozone analysis. All connecting lines were 1/4 inch OD aluminum or teflon tubing (Figure 1).

Ozone was produced from dry zero grade oxygen containing less than 1 molar ppm mg/l hydrocarbon. Helium used in flushing ozone from the reactor was also zero grade. Nitrogen used in stripping TOC samples was ultra high purity. All other chemicals were ACS reagent grade.

Analytical equipment included a Corning pH meter (Model 12), a Beckman DU-2 spectrophotometer, a Technicon Autoanalyzer, and a Beckman Carbonaceous analyzer, Model 915. Gas volume measurements were read on wet test meters from Precision Scientific Company. Ozone concentrations were determined by the iodometric method (17). Because of the high concentrations of ozone, the ozonated KI solution was diluted to three

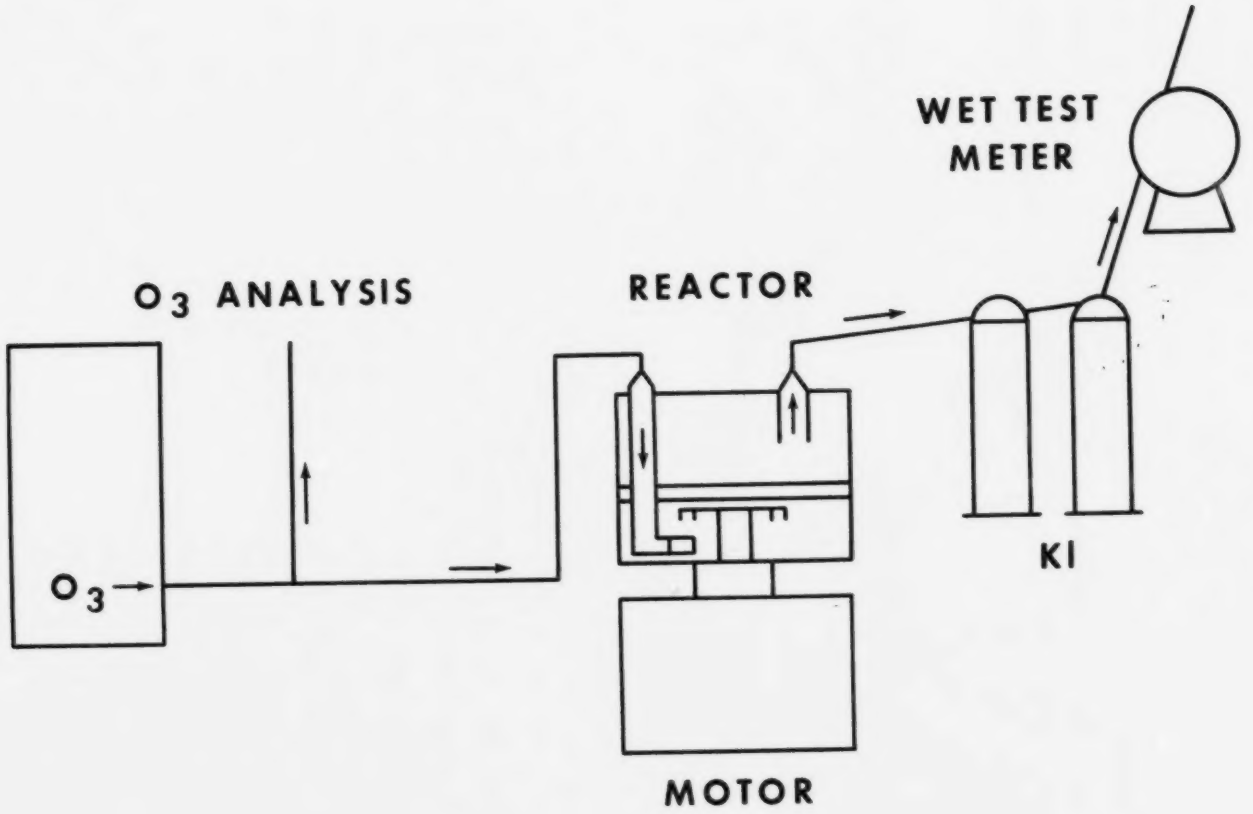

Figure 1. Ozonation System

fourths of a known volume, acidified with 1N H_2SO_4 and brought to volume. An aliquot of the diluted KI solution was then titrated with 0.1N sodium thiosulfate.

Ammonia (18) and nitrate + nitrite (19) were determined on a Technicon Auto Analyzer. Total Organic Carbon (TOC) was measured on a Beckman Carbonaceous Analyzer (20). The COD, BOD, and TKN analyses employed Standard Methods (21).

SECTION V

ORGANIC OXIDATION

Repetitive ozonation of the various wastewaters revealed that variable ozone transfer occurred in the laboratory tests for the same contact time, ozone dosage, and experimental conditions. The ozone transfer varied with the organic content of the water, not only in wastewaters of different types, but with different samples of the same wastewaters. Thus, the maximum applied ozone dose at the maximum experimental contact time of 90 minutes varied not only with type of wastewater but also within different samples of the same type. The organic removals (TOC and COD) presented, however, were typical of wastewater types.

When unfiltered raw wastewater containing high suspended solids and dissolved organic material was treated with increasing ozone doses, the total COD gradually decreased by 50% to a residual of 159 mg/l at the maximum (90 minute contact time) applied ozone dose of 325 mg/l (Figure 2). Ozonation at the maximum dose removed 73% of the BOD_5 (Figure 2). At the maximum ozone dose, the removal of total organic carbon (TOC) in the raw wastewater was 36% with a residual of 60 mg/l TOC (Figure 2). As the end product of organic carbon oxidation is CO_2, the removal of TOC indicated that portions of the organics were oxidized to CO_2.

In the raw wastewater, COD, BOD_5 and TOC residuals continued to decrease sharply with increasing ozone doses (and contact time) revealing that additional easily oxidizable organic compounds remained in the wastewater at the maximum applied ozone dose.

In contrast to raw wastewater, oxidation of the organics in treated wastewaters required much lower and potentially practical ozone dosages. Ozonation of a high quality secondary effluent at the maximum applied

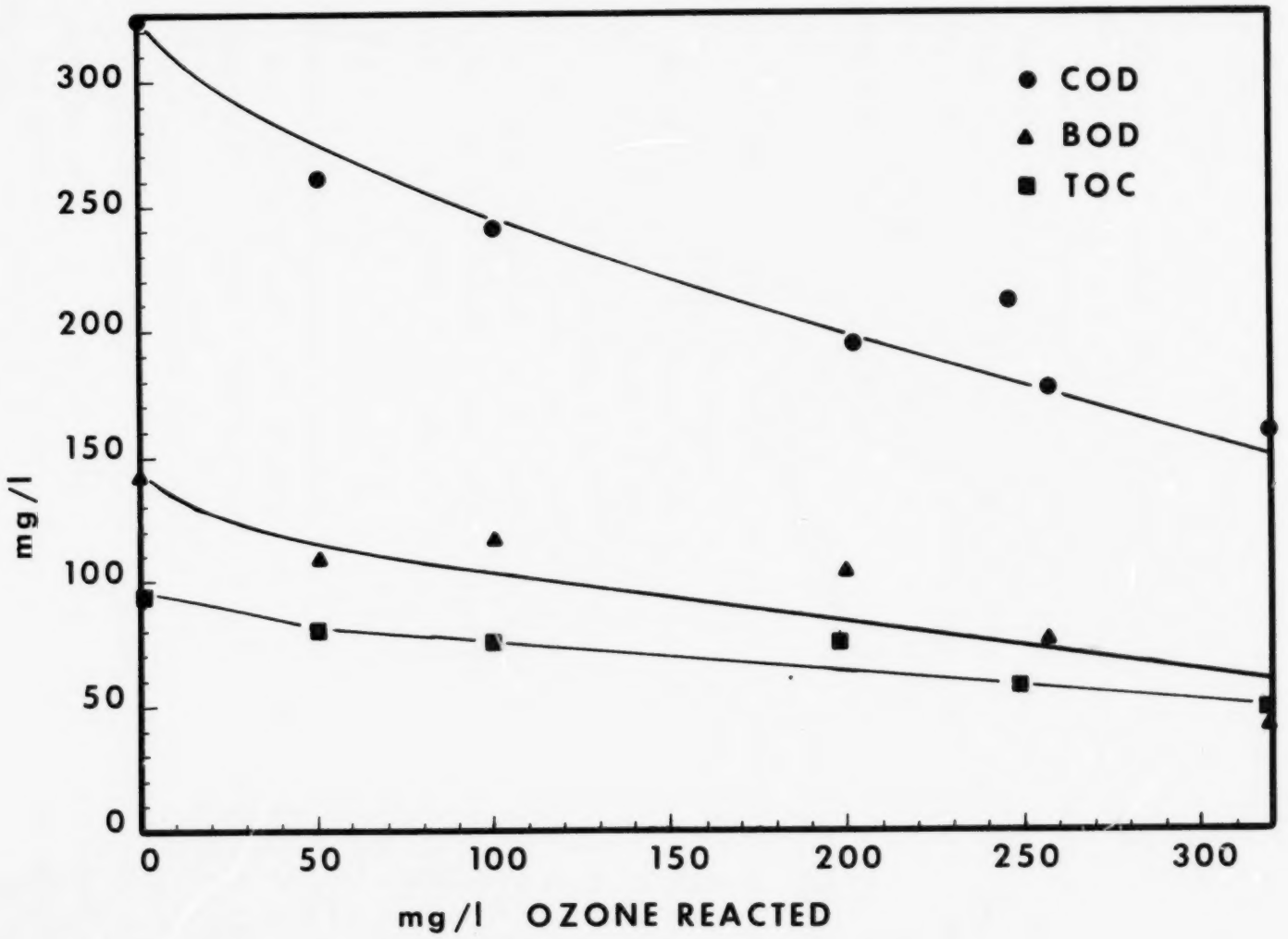

Figure 2. Ozonation of Raw Wastewater

ozone dose (90 minutes of contact) of 258 mg/l ozone reduced the COD by 81% to a residual COD of 7 mg/l (Figure 3). An ozone dose of approximately 60 mg/l, however, reduced the residual COD to less than 10 mg/l for about 70% removal.

The rate of COD removal occurred rapidly only at low ozone doses (60 mg/l). At higher ozone doses in the secondary effluent (60-258 mg/l) the slow decrease in COD per unit of added ozone (or time) indicated the presence of organic material that was difficult to oxidize.

Ozonation completely removed the BOD_5 from the secondary effluent (Figure 3), but required an ozone dose of 210 mg/l. At the 60 mg/l ozone dose, the BOD_5 was reduced by 58% to 5 mg/l. The TOC decreased by 60% to a residual of 6 mg/l (Figure 3) at the maximum ozone dose. At the 60 mg/l ozone dose, the residual TOC was reduced by 36% to 13 mg/l.

Ozonation of typical lime clarified and filtered secondary effluents exhibited similar COD removals as the secondary effluent (Figure 4). The COD removed from the lime clarified and filtered secondary effluent exceeded 93% with a residual COD of 3.4 mg/l at maximum applied ozone dose of 307 mg/l (Figure 4). An ozone dosage of 100 mg/l, however, reduced the COD from 45 mg/l to 12 mg/l (approximately 70% removal). Above 70% of COD removal, the rate of COD reduction per unit ozone began to decrease sharply. Ozonation completely removed the BOD_5 from the lime clarified and filtered secondary effluent at the maximum applied ozone dosage of 397 mg/l and reduced the BOD to approximately 4 mg/l at the 100 mg/l ozone dosage (Figure 4). The TOC at the 100 mg/l ozone dosage (70% COD reduction) was reduced from 21 mg/l to less than 10 mg/l.

In typical lime clarified and filtered D.C. raw wastewater, the COD removal was 73% with a residual COD of 13 mg/l at a maximum applied ozone dose of 104 mg/l (Figure 5). The BOD was completely removed at the

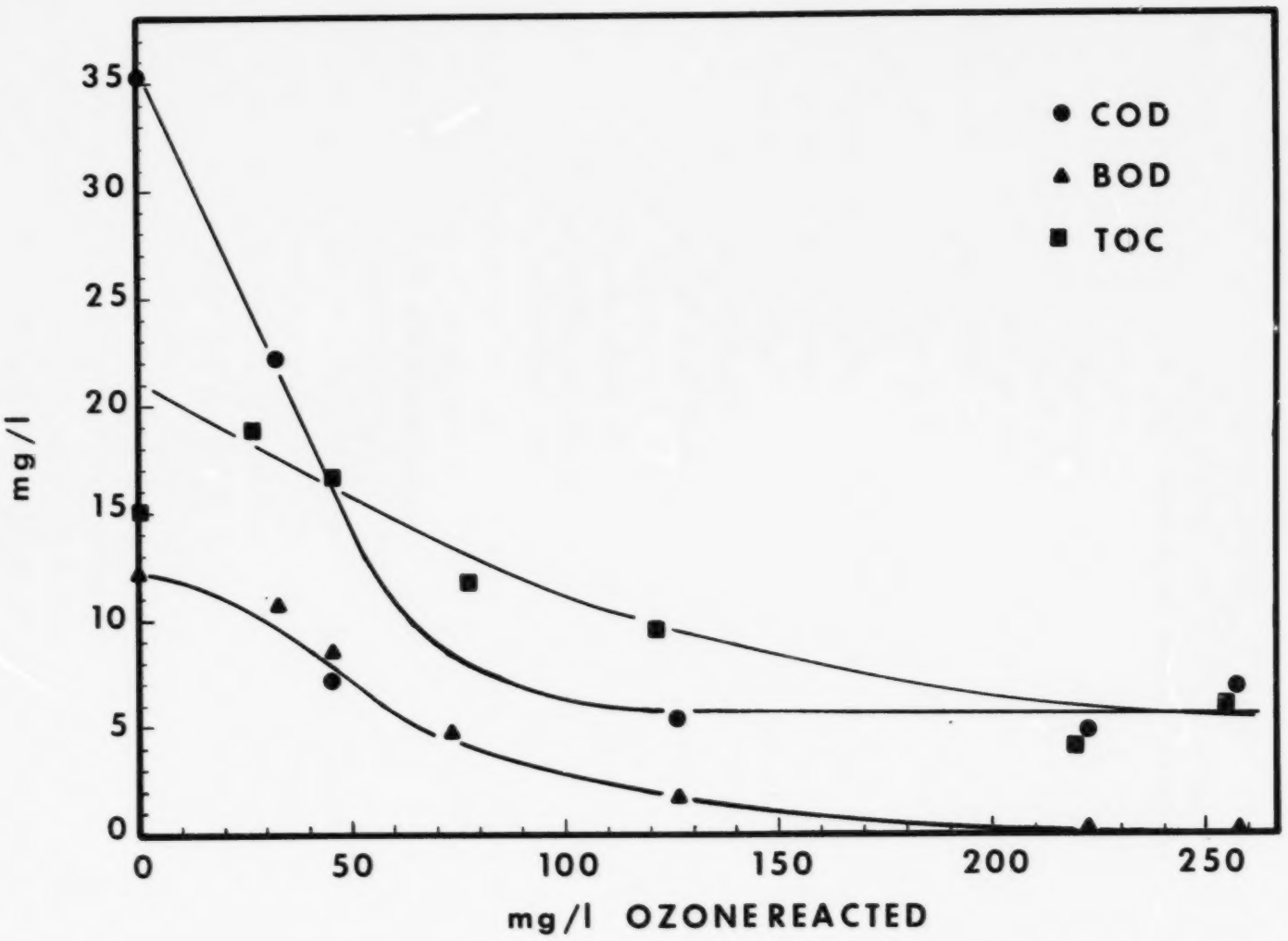

Figure 3. Ozonation of Secondary Effluent

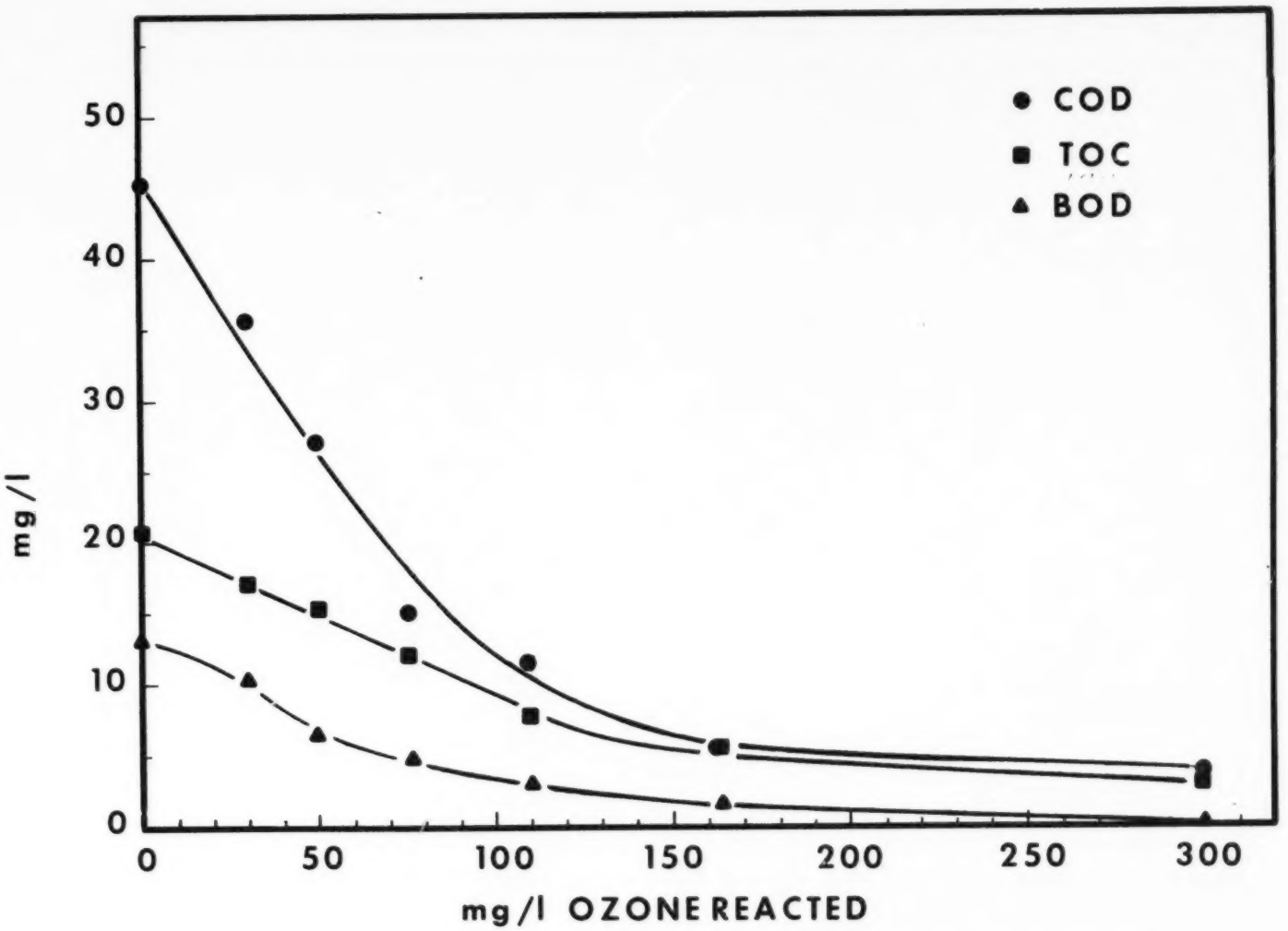

Figure 4. Ozonation of Lime Clarified and Filtered Secondary Effluent

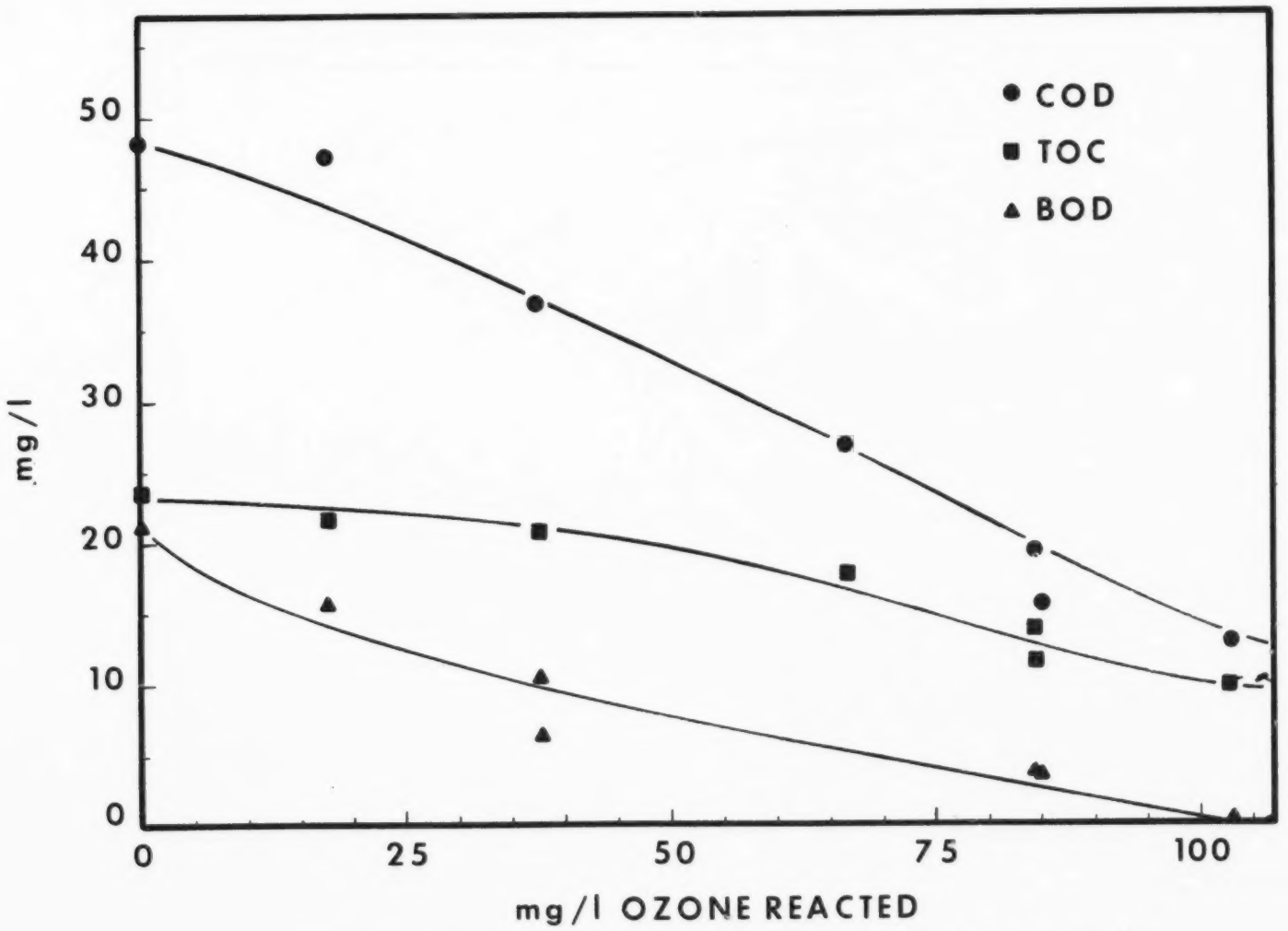

Figure 5. Ozonation of Lime Clarified and Filtered Raw Wastewater

maximum applied ozone dose of 104 mg/l. TOC removals gradually increased to 58% removal at the maximum applied ozone dose to a residual of 10 mg/l (Figure 5).

Ozonation of carbon column effluents from physical-chemical treatment of raw wastewater with low initial COD's exhibited a COD removal of 90% with a residual COD of 1.3 mg/l at a maximum applied ozone dose of 151 mg/l (Figure 6). A COD residual of 3.7 mg/l, however, was achieved with a 50 mg/l ozone dose. The BOD_5 was also essentially removed at the 50 mg/l ozone dose (Figure 6). The TOC removal was 44% at a 50 mg/l ozone dose with a residual TOC of 3.8 mg/l. The TOC residual decreased very little with increasing ozone doses above the 50 mg/l ozone dose.

While repetitive tests on the lime clarified and filtered effluents revealed that variable ozone transfer occurred with time for the same type of effluent and experimental conditions, more ozone was generally transferred in a given time to secondary and to lime clarified and filtered secondary effluents than to lime clarified and filtered raw wastewater or to carbon column effluents from physical-chemical treatment of raw wastewater (Table 1). The reason for the difference in transfer efficiency between the biologically treated and physical-chemical effluents was not determined.

The effectiveness of ozone for removing COD was described using the organic oxidation efficiencies (equation 1). The organic oxidation efficiencies based upon 1 available oxygen atom per molecule of ozone for COD removal in raw wastewater and in secondary effluents (Figure 7) exceeded 100% (356% for raw wastewater and 280% for secondary effluent). The high organic oxidation efficiencies observed in raw wastewaters and secondary effluents at high COD/O_3 ratios revealed that either molecular oxygen or the entire ozone molecule was involved in the initial oxidation of the organics. The efficiencies, however, decreased as the ozone dose

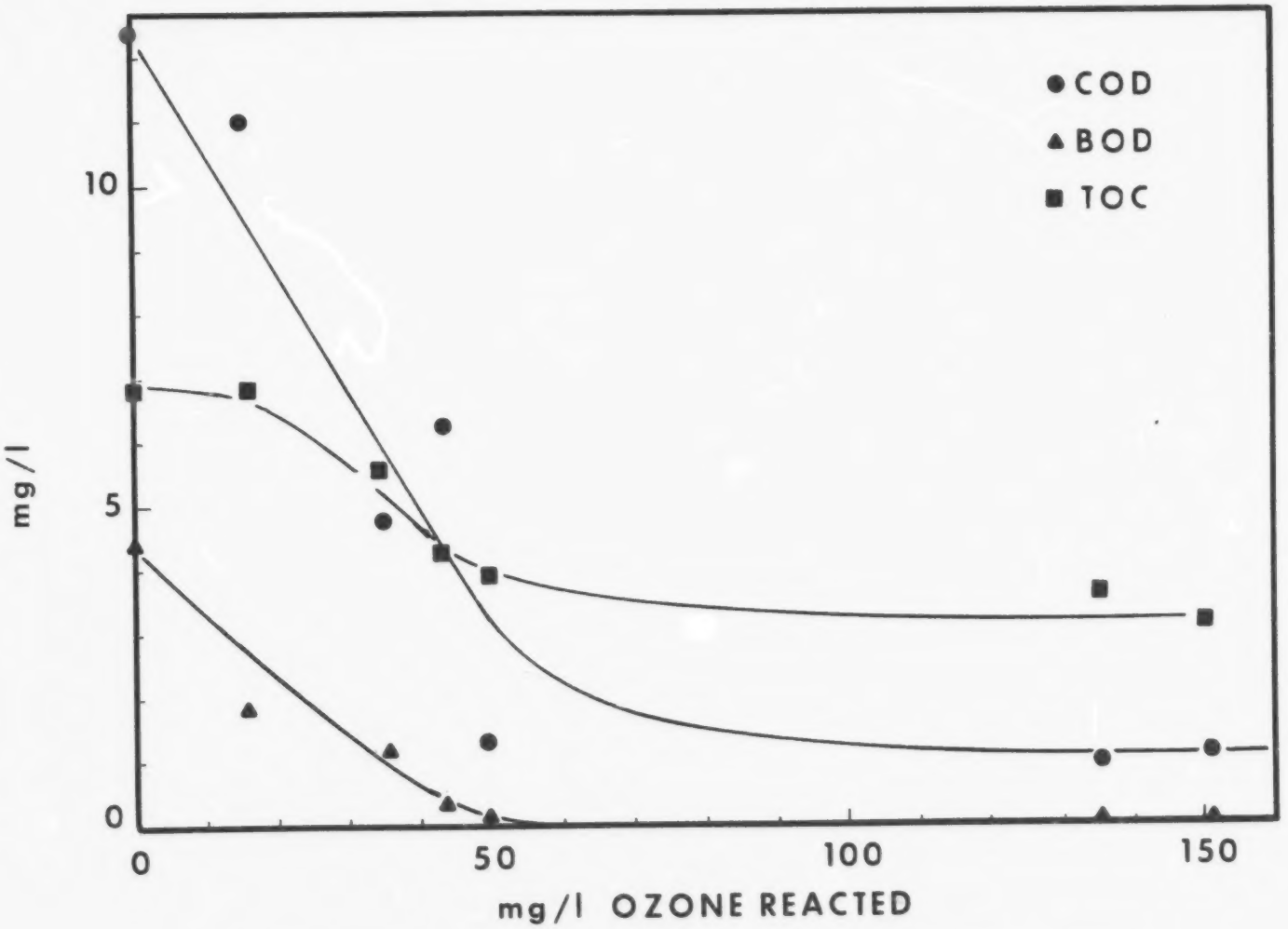

Figure 6. Ozonation of Effluent from Carbon Column Physical-Chemical Treatment of Raw Wastewater

TABLE 1

OZONE ORGANIC OXIDATION EFFICIENCIES

IN

VARIOUS WASTEWATERS

EFFLUENT	70% REMOVAL OF COD		OZONE TRANSFERRED IN 90 MINUTES	
	RESIDUAL COD mg/l	mg/l of OZONE TRANSFERRED	O.O.E.%	mg/l
RAW	97	510*	130*	325
SECONDARY	10.6	60	124	285
RAW LIME	13	104	102	104
LIME SECONDARY	13	95	101	300
CARBON COLUMN	3.7	47	55	150

* Extrapolated value (O_3 required to achieve 70% reduction in COD within the 90 minutes of contact time employed in the study).

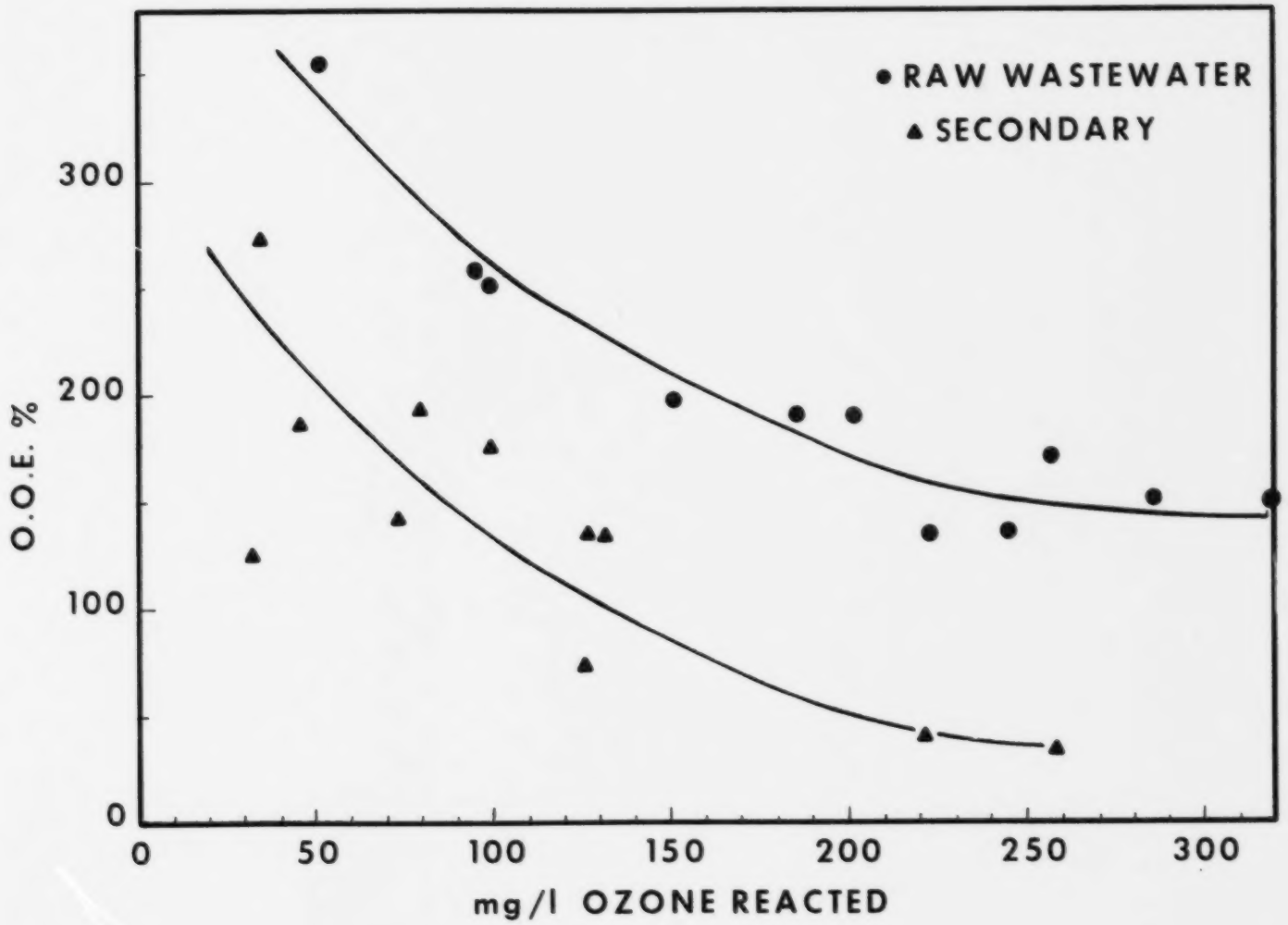

Figure 7. Organic Oxidation Efficiency in Raw and Secondary Wastewaters

increased and at the maximum applied ozone dose, the efficiencies were approximately 150% in raw wastewater and 33% in the secondary effluent. Ozonation of other raw wastewaters produced organic oxidation efficiencies at low ozone dosages (high COD to applied ozone) exceeding 700%. In contrast to the raw wastewater and secondary effluent, organic oxidation efficiencies for COD removal in lime clarified and filtered raw and secondary effluents (Figure 8) initially varied little with ozone dosage, averaging approximately 100% until the COD removal increased above 70% (100 mg/l ozone). Then the organic oxidation efficiencies gradually began to decrease and indicated the presence or formation of an oxidation resistant residual organic material.

Organic oxidation efficiencies of carbon column effluent from physical-chemical treated raw wastewater (Figure 8) were lower than those in clarified effluents. With low initial COD's of the carbon column effluent, the organic oxidation efficiencies averaged approximately 50% until the COD removal increased above 70% (50 mg/l ozone dose). Then the efficiencies gradually decreased to approximately 20% at the maximum applied ozone dose.

With the 90 minute contact time system previously described, 70% COD removal could not be achieved in the raw wastewater samples. The organic oxidation efficiencies (Table 1) at 70% COD removal were approximately 130% in the raw wastewater (extrapolated), 124% in secondary, 101% in lime clarified and filtered secondary effluent, 102% in lime clarified and filtered raw wastewater, and 55% in the carbon column effluent. In all effluents, further addition of ozone beyond 70% COD removal produced inefficient COD reduction with a sharp decrease in organic oxidation efficiency, and therefore, further ozonation after 70% COD removal was not practical for COD reduction.

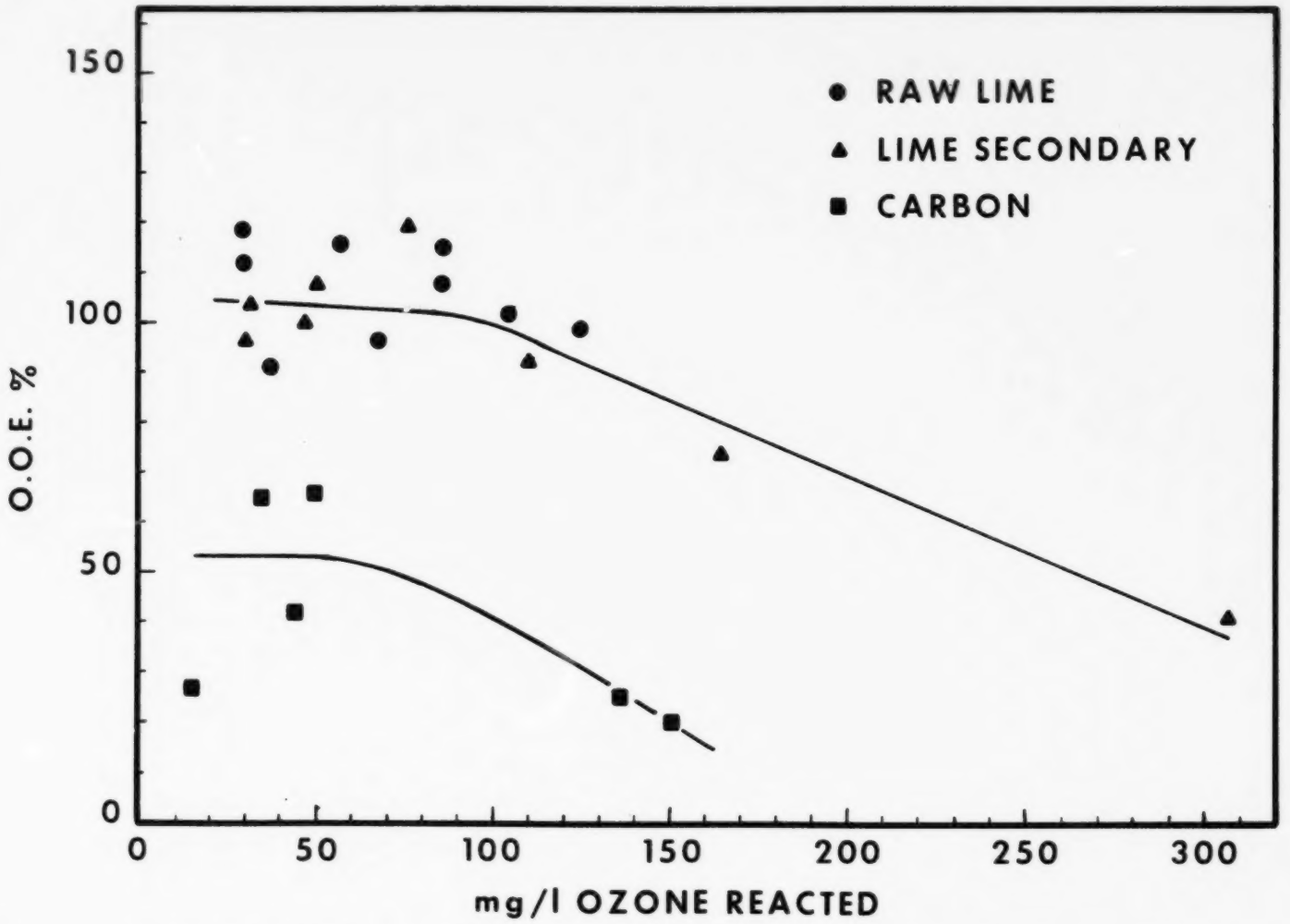

Figure 8. Organic Oxidation Efficiency in Lime Clarified and Filtered Secondary Effluents, Lime Clarified and Filtered Raw Wastewater and Carbon Column Effluents

SECTION VI

NITROGEN OXIDATION

The literature (22) indicated that ozone reacted with organic nitrogen (amino acids and proteins) to liberate ammonia. In this study, the ozonation of wastewaters oxidized the total kjeldahl nitrogen (TKN) (Figures 9, 10, 11, 12, and 13) including both organic nitrogen and free ammonia. The liberated ammonia from the organic nitrogen and original dissolved ammonia reacted with ozone to form NO_3^- -N.

In the raw wastewater and lime clarified and filtered raw wastewater with high organic nitrogen content, however, nitrate production did not always stoichimetrically correspond to the oxidation of the TKN (Figures 9 and 10). Thus oxidation of organic nitrogen did not necessarily go completely to nitrate. In secondary effluent, lime clarified and filtered secondary effluent, and in carbon column effluents, with little organic nitrogen, ammonia oxidation corresponded nearly stoichimetrically to the amounts of NO_3^- produced (Figures 11, 12, and 13) (Table 2).

In general, for any given ozone dose, the lower the initial COD in the wastewater (that is, increased pretreatment), the greater was the oxidation of TKN. As an example, 100 mg/l ozone, in raw wastewater containing an initial COD of 325 mg/l (Figure 9), oxidized 3 mg/l TKN (14% TKN removal) while in a carbon column effluent containing an initial COD of 14.2 mg/l, an ozone dose of 100 mg/l reduced the TKN by 5.2 mg/l or 53% (Figure 13). In all the effluents, however, NO_3^- formation occurred slowly in contrast to the rapid removal of COD until 70% of the COD was removed.

The ratio of ozone used in nitrate formation to the ozone used for removal of the COD (Table 3) revealed the importance of the nitrogen demand on COD reduction especially in wastewaters with low initial COD. The oxygen

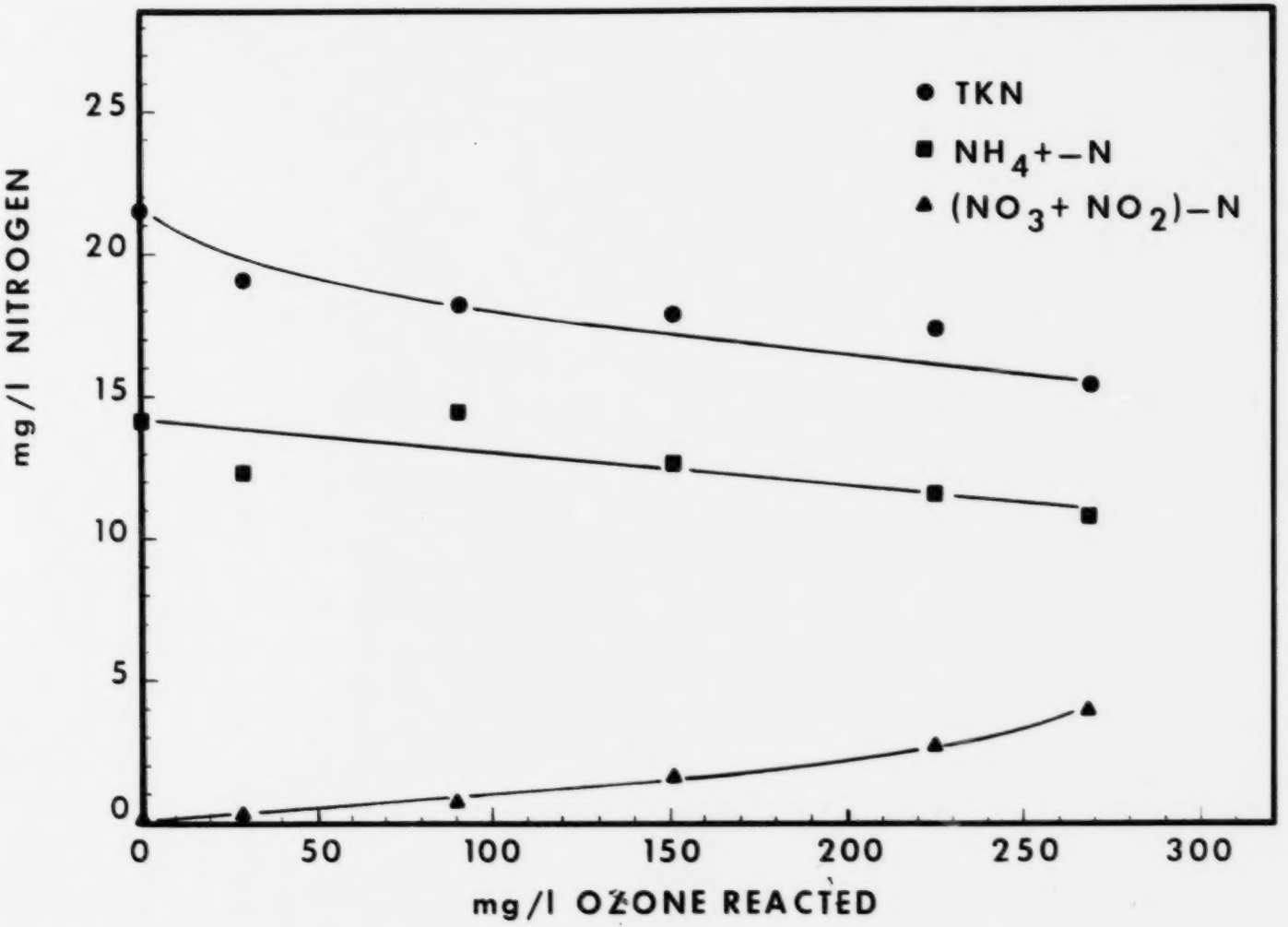

Figure 9. Oxidation of Nitrogen in Raw Wastewater

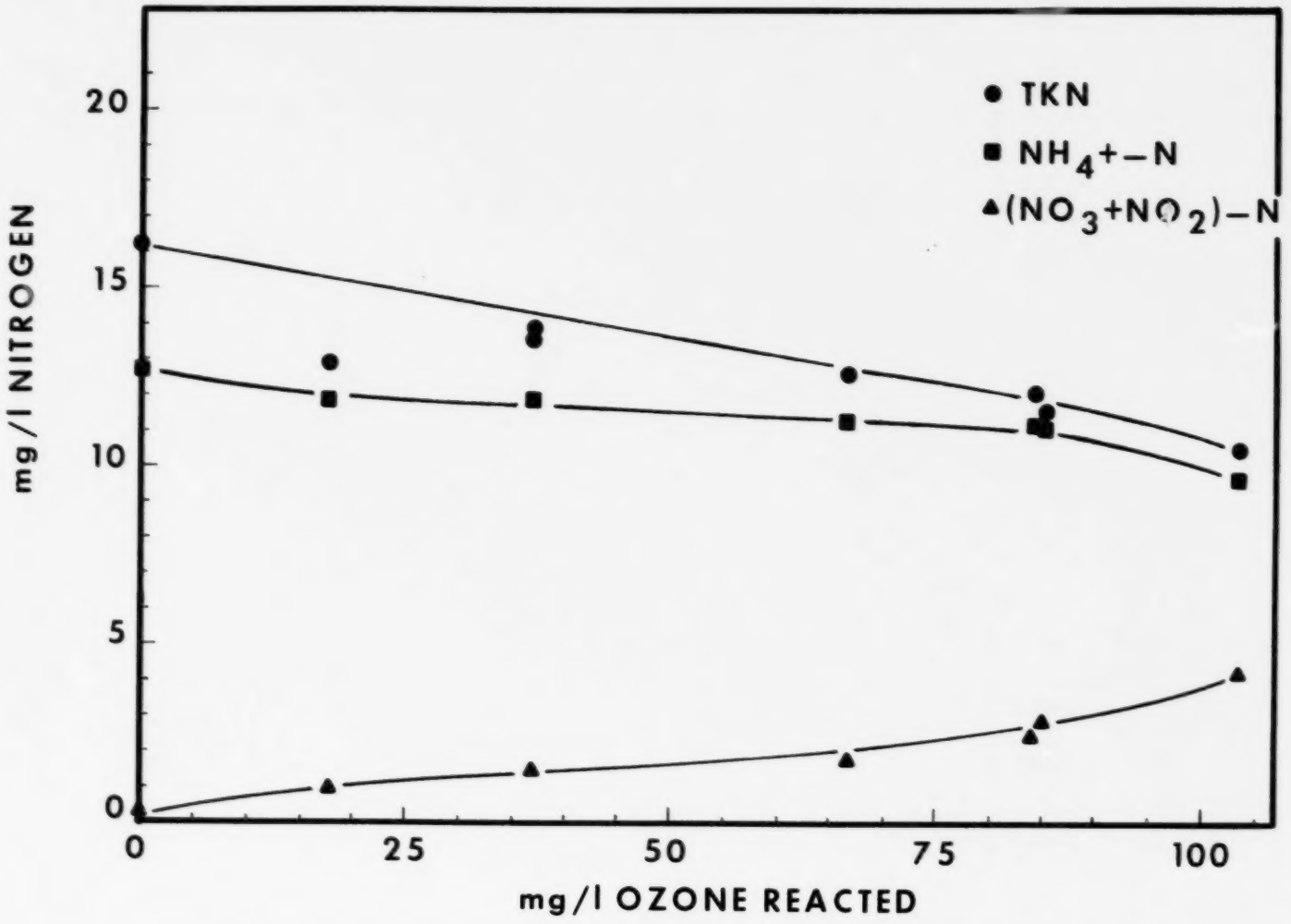

Figure 10. Oxidation of Nitrogen in Lime Clarified and Filtered Raw Wastewater

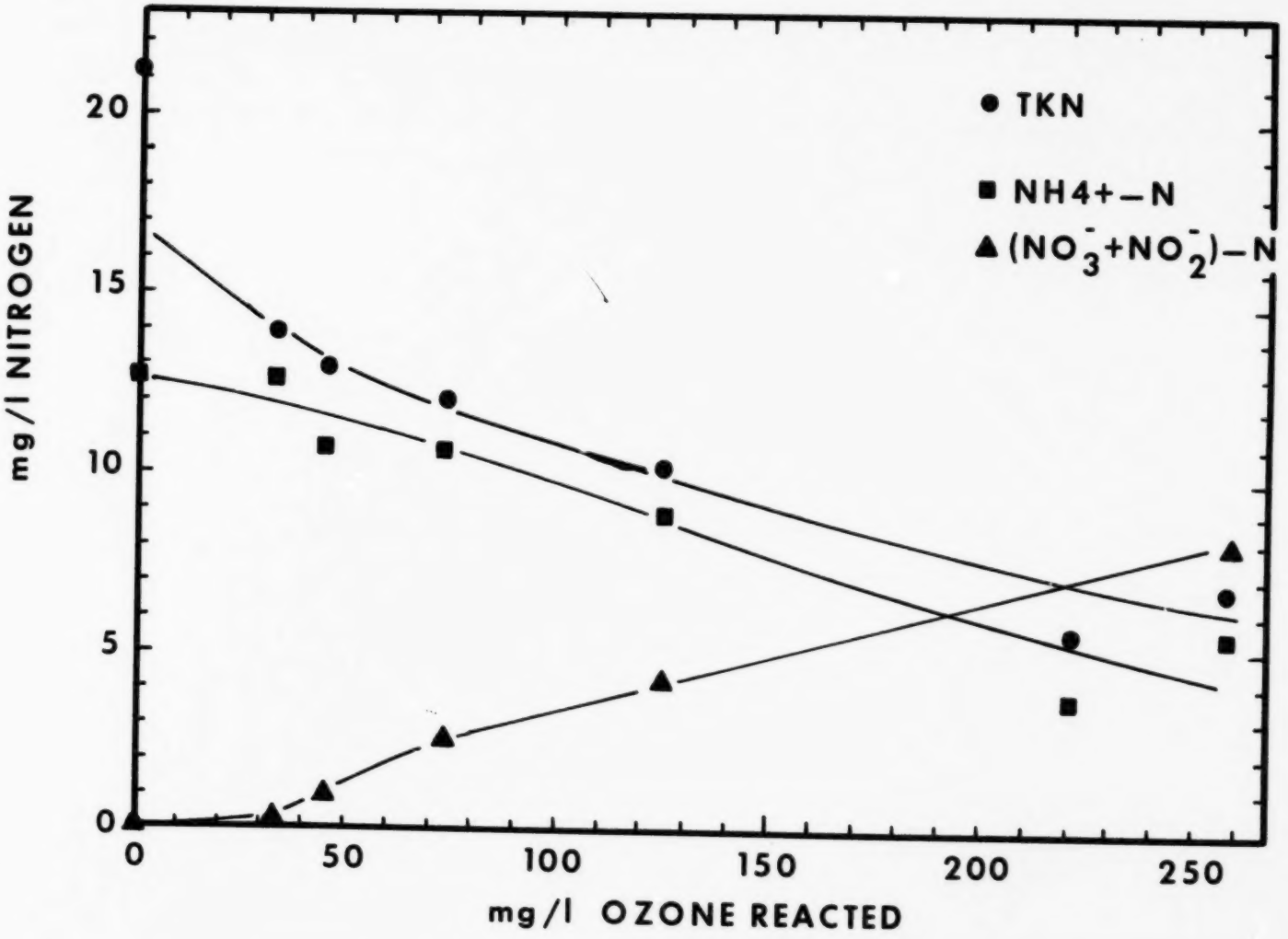

Figure 11. Oxidation of Nitrogen in Secondary Effluent

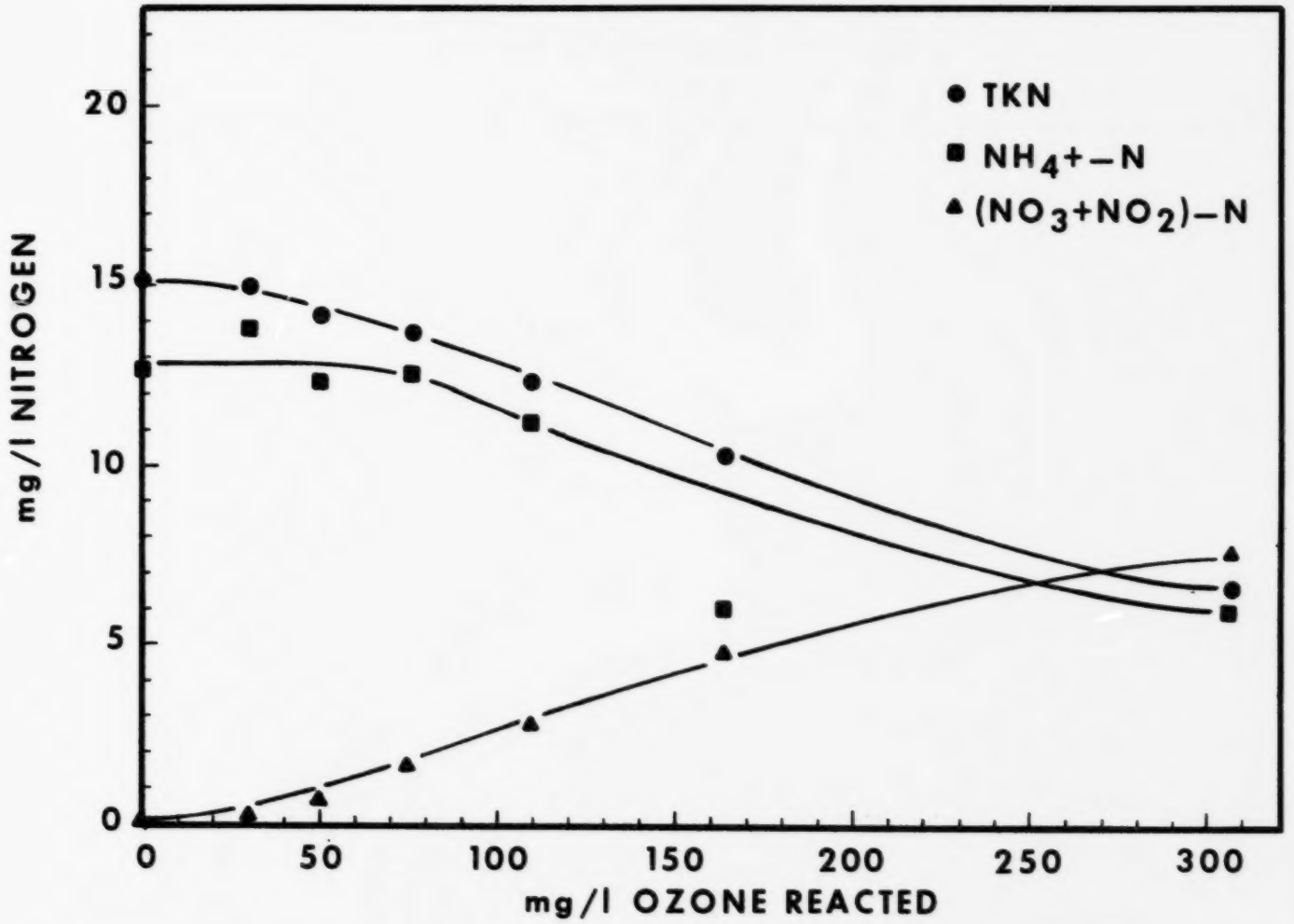

Figure 12. Oxidation of Nitrogen in Lime Clarified and Filtered Secondary Effluent

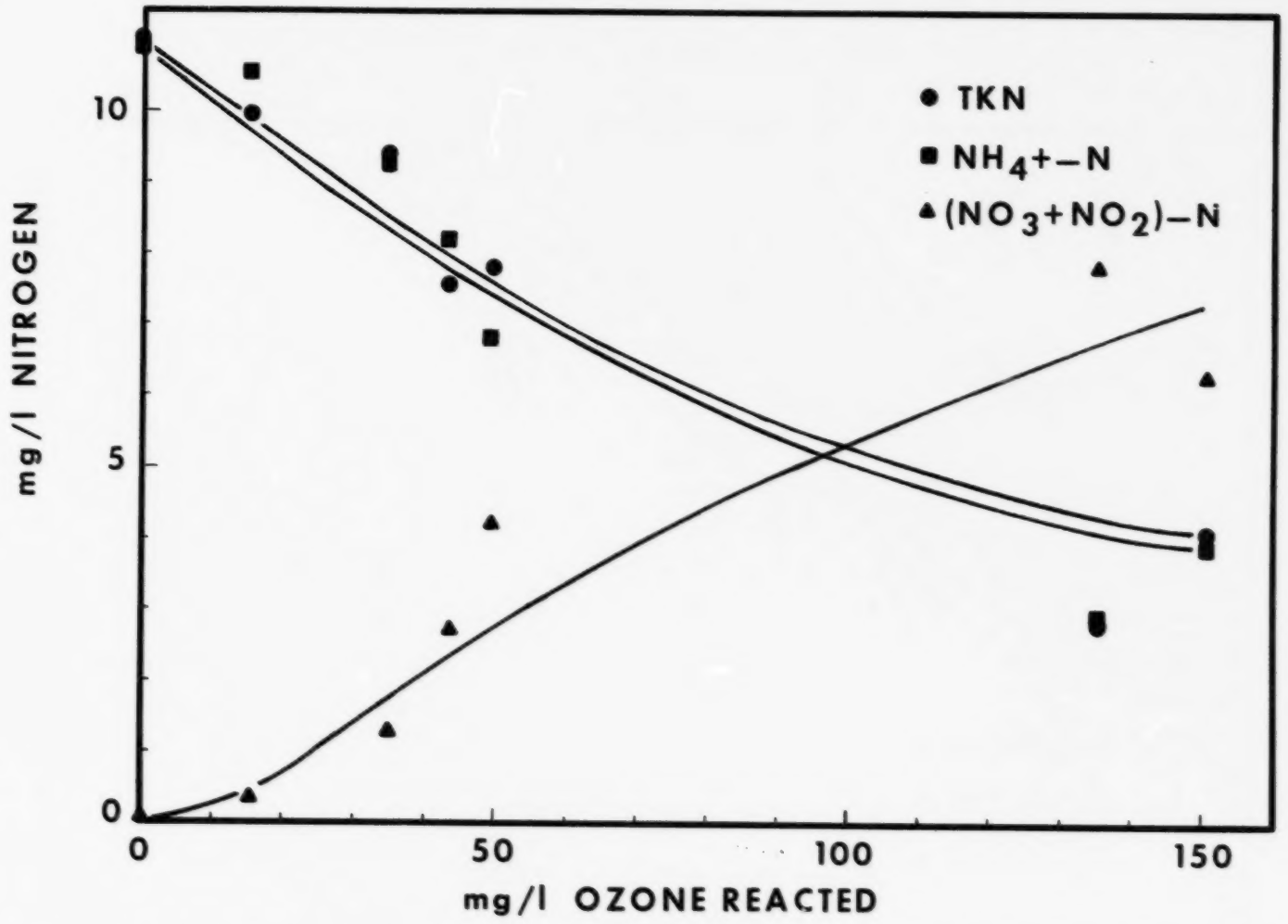

Figure 13. Oxidation of Nitrogen in Carbon Effluents from Physical-Chemical Treatment

TABLE 2

TYPICAL NITROGEN CONCENTRATIONS

mg/l ozone reacted	TKN mg/l	NH_4^+ mg/l	$(NO_3^- + NO_2^-)$ mg/l
Raw Wastewater			
0	21.5	14.0	0
100	18.0	13.0	1
Secondary			
0	14.4	12.0	0
100	9.6	9.4	3.8
Lime Clarified and Filtered Secondary			
0	15.2	12.6	0
100	12.9	11.6	2.6
Carbon Column			
0	11.0	10.9	0
100	5.3	5.08	5.4

TABLE 3

TOTAL AND ORGANIC OXIDATION EFFICIENCIES

EFFLUENT	OXYGEN DISTRIBUTION RATIO	70% COD REMOVAL	
	$\frac{NOD}{COD}$	ORGANIC O.E.%	TOTAL O.E.%
RAW	.07	150	162*
SECONDARY	.27	124	151
RAW LIME	.34	102	140
LIME SECONDARY	.27	101	129
CARBON	1.68	55	155

* Extrapolated value (ozone required to achieve 70% COD reduction could not be applied within the 90 minute maximum contact time employed in the study).

distribution ratio between NOD and COD during ozonation and the COD removals as a function of ozone dose suggested that the relative order of oxidation was; easily oxidizable organic material, TKN, and slowly oxidizable (nearly refractory) organic material.

Ozonation of carbon column effluents from physical-chemical treatment of raw wastewater which had been breakpoint chlorinated (and dechlorinated) for ammonia removal, and ozonation of the carbon column effluents with the ammonia revealed the oxidation of ammonia nitrogen before the organic nitrogen (Figure 14). For example, in the non-chlorinated carbon column effluent, NH_4^+ -N removals corresponded to approximate stoichiometric increases in NO_3^- -N, while the organic nitrogen concentration remained constant. In the chlorinated waters (without NH_4^+ -N), the organic nitrogen was oxidized to NO_3^- -N (Figure 14). Thus, the complete relative order of oxidation was easily oxidizable organics (COD), ammonia, organic nitrogen, and slowly oxidizable (nearly refractory) organic material.

In the studies on physical-chemical treatment effluents, ozonation of carbon column effluents of low initial COD required greater amounts of ozone for the removal of COD and TOC than was required in the same waters without ammonia (Figure 15). For example, in non-chlorinated carbon column effluent (with ammonia), a COD removal of 40% was achieved with a residual COD of 6.7 mg/l at an applied ozone dose of 50 mg/l. In the same carbon column effluent, after breakpoint chlorination (ammonia free), a 55% COD removal was attained with a residual COD of 5.0 mg/l at the same applied ozone dosage. The TOC removals also required less ozone in the absence of ammonia (Figure 15). For example, in the breakpoint chlorinated carbon column effluent, an applied ozone dose of 40 mg/l was required for a 60% TOC removal to a residual of 2.5 mg/l TOC. The same non-chlorinated effluent (with ammonia) required an applied ozone dosage of 90 mg/l to achieve the 2.5 mg/l TOC residual. It should be noted,

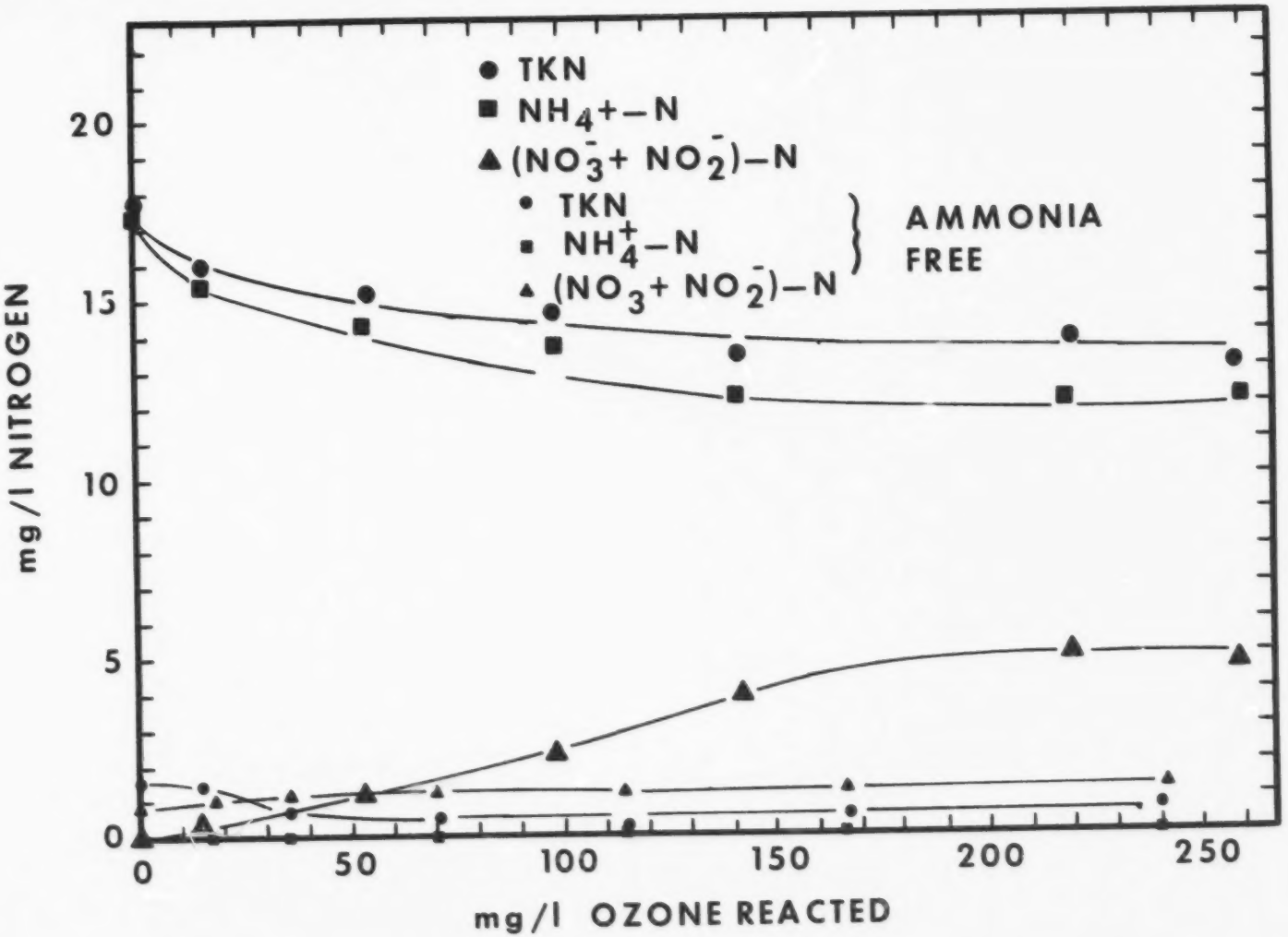

Figure 14. Oxidation of Nitrogen in Carbon Column Effluents Before and After Ammonia Removal

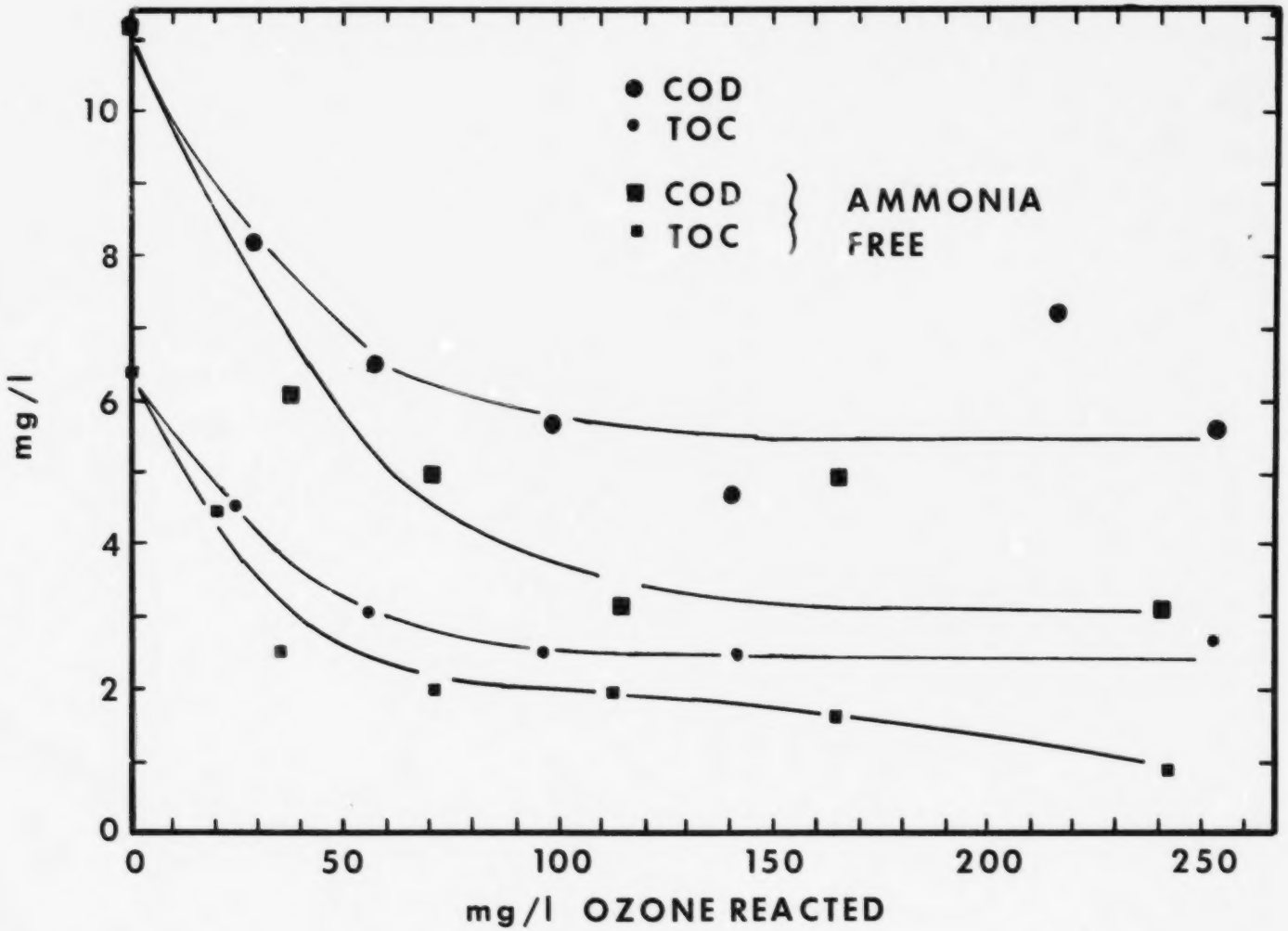

Figure 15. Ozonation of Carbon Column Effluents Before and After Ammonia Removal

however, that even with the ammonia and organic nitrogen essentially removed, the residual COD was only very slowly oxidized after appreciable exposure to additional ozone. The removal of the nitrogen did not permit complete oxidation of the residual organics.

Complete evaluation of the oxidation capabilities of ozone must account for ozone consumed in nitrogen oxidation. Total oxidation efficiencies (equation 2) after five minutes of ozonation did not significantly differ from the organic oxidation efficiencies, because in all wastewaters, less than 1 mg/l of nitrate was produced with high COD/O_3 ratios.

After removal of 70% of the COD, total oxidation efficiencies for organic and ammonia oxidation (Table 3) in all treated effluents were significantly higher than oxidation efficiencies based on COD removal alone, and were greater than 100%. As an example, the organic oxidation efficiency for carbon treated effluents at 70% COD removal was 55%, while the total oxidation efficiency was 155%. These total oxidation efficiencies confirm that either oxygen from molecular oxygen or the entire ozone molecule was involved in the oxidation mechanism, and strongly suggested that contributions to the oxidation process include an autoxidation (molecular oxygen) mechanism.

SECTION VII

pH EFFECTS

Aliquots of secondary effluent were ozonated at pH 5, 9 and 11 for 60 minutes. The ozone transferred at pH 5 was 38 mg/l, at pH 9, 160 mg/l and at pH 11, 256 mg/l. Thus, the transfer of ozone increased with increasing pH.

At pH 5, a 14% COD removal occurred with a 50% organic oxidation efficiency (Table 4). At pH 9, the COD removal was 57% with a 55% organic oxidation efficiency, and at pH 11, the COD removal was 60% with a 34% organic oxidation efficiency. Similarly the TKN at pH 5, 9 and 11 were reduced by 1%, 52% and 90% with residuals of 16.6 mg/l, 8.8 mg/l and 0.5 mg/l, respectively. Total oxidation efficiencies (organic and nitrate) were: 58.8% at pH 5, 93.3% at pH 9 and 82.1% at pH 11 (Table 4).

At pH's 5 and 9, TKN removals correspond to an approximate stoichiometric increase in NO_3^-. The TKN removed at pH 11 was 15.4 mg/l but only 11.9 mg/l NO_3^- -N was detected. The difference between the NH_3 removed and the nitrate produced was likely caused by oxygen stripping of ammonia from the wastewater at pH 11.

Thus, the study revealed the pH range for optimum COD removal was between 7 and 9. The literature indicated that ozone in acid solution is more stable with slower decomposition rates. In this study, the ozone produced the least COD oxidation at pH 5. At pH's above 9, the nitrogen oxidation increased. For example, at the maximum applied ozone dose, the nitrogen oxygen demand for ozone in secondary effluent was 7.7 mg/l ozone at pH 9, and 13.6 mg/l ozone at pH 11 (Table 4).

TABLE 4

OZONATION AND pH

pH	mg/l of OZONE REACTED IN 60 MINUTES	O.E.%	% REMOVAL			$(NO_3 + NO_2)$ -N mg/l
			COD	TKN	NH_4^+	
5	38	50	14	1	3	0.35
9	160	50	57	52	55	6.75
11	256	34	60	90	97	11.90

SECTION IX

REFERENCES

1. Hann, V.A., "Disinfection of Drinking Water with Ozone", Jour. AWWA, 1316 (1956).
2. O'Donovan, D.C., "Treatment with Ozone", Jour. AWWA, 57, 1167, September 1965.
3. Ozonation treatment shown. Water and Wastes Engineering, 8, 8 January 1971.
4. Stumm, Werner, "Ozone as a Disinfectant for Water and Sewage." Boston Society of Civil Engineers, 68, October 1957.
5. Diaper, E.W.J., "Microstraining and Ozonation of Water and Wastewater." Water and Wastes Engineering, 5, 56, February 1968.
6. Campbell, R.M., and M.B. Pescad, "Ozonation of Turret and other Scottish Waters", Water and Sewage Works, 113, 268, July 1966.
7. Thirumurthi, D., "Ozone in Water Treatment and Wastewater Renovation", Water and Sewage Works, 115:R, 106, November 29, 1968.
8. Palin, A.T., "The Ozonation of Water with Special Reference to Color Removal", Water and Wastes Engineering, 56, 271 (1953).
9. Masse, A.E., "Successful Odor Control at Michigan Wastewater Treatment Plant", Water and Sewage Works, 114, 322, September 1967.
10. Miller, F.J., "Upline Sewage Treatment Eliminates Odors, Reduces BOD, Cuts Complaints", Water and Wastes Engineering, 3, 52, December 1966.
11. Sewage Plant in Center of Town is Ozonized and Soundproofed, Engineering News, 172, 34, June 11, 1964.
12. Pateman, S.G., "Oxnard Sewage Plant Solves Odor Control Problem", Water and Sewage Works, 116, 352, September 1969.
13. Eisenhauer, H.R., "Oxidation of Phenolic Wastes", WPCF Jour., 36, 1116, September 28, 1964.
14. Cronan, C.S., Ozone Counters Waste Cyanides "Lethal-Punch", Chem. Engineering, 65, 63, March 24, 1958.

15. Labine, R.A., "Phenol-Free Wastewater", Chemical Engineering, 66, 114, August 24, 1959.
16. "Ozone Treatment of Secondary Effluents from Wastewater Treatment Plants", Huibers, A., R. McNabney, and A. Halfon, Report No. TWRC-4, U.S. Department of the Interior, Federal Water Pollution Control Administration, Cincinnati, Ohio, April 1969.
17. "Standard Methods for the Examination of Water and Wastewater", 12 ed., American Public Health Association, New York, 1965.
18. "FWPCA Methods for Chemical Analysis of Water and Wastes", U.S. Department of the Interior, Federal Water Poll. Control Adm., Cincinnati, Ohio, November 1969.
19. Kamphake, L. et al., "Automatic Analysis for Nitrate by Hydrazine Reduction", Water Res., 1, 205, 1967.
20. Schaeffer, R.B., et al, "Application of a Carbon Analyzer in Waste Treatment", Journal Water Poll. Control Fed., 37, 1545, 1965.
21. Ob. cit. (17)
22. Mudd, J.B., et al, "Reaction of Ozone with Amino Acids and Proteins", Atmospheric Environment, 3, 669, November 1969.
23. Bishop, D.F., et al, "Physical-Chemical Treatment of Municipal Wastewater", U.S. Dept. of the Interior, Fed. Water Quality Adm., Cincinnati, Ohio, October 1970.